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NYO-531

THE MOLECULAR SPECTRA OF TRITIUM
AND RELATED SPECTRA

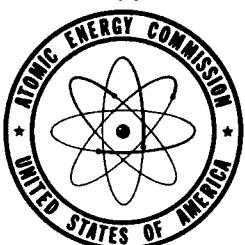
Annual Report

By

G. H. Dieke

November, 1950

Johns Hopkins University



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1. Summary:

The photography and wave-lengths measurements and analysis of the TH and T₂ spectrum proceeded largely as planned. Some work was also done on the D₂ spectrum. In the analysis of complicated parts of the spectra a modification of the spectrum in a discharge through 200 mm helium and traces of T₂, D₂ or TH was very helpful. This modified spectrum showed only bands originating from vibrationless levels at a high rotational temperature.

Attempts to obtain the spectrum of T₂ free from TH and H₂ so far have not been successful, and a modification in the discharge tube is proposed. This modified tube should also be satisfactory for accurate intensity measurements.

The analysis of the molecular spectrum of He revealed a noticeable interaction between nuclear spin and orbital angular momentum.

The relative intensities of H_α and T_α can be used to determine spectroscopically the relative concentration of tritium. Experiments have been made and are still in progress to determine which factors in the discharge condition other than the tritium concentration will modify the H_α/T_α ratio. This will show under which conditions the spectroscopic determination of deuterium and tritium concentrations will give reliable results.

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The Molecular Spectra of Tritium and Related Spectra

In the Annual Report for 1949 (JHU-4) the program for the work to be carried out on this project was outlined. During 1950 the work went ahead mainly in concordance with this program. The account of those parts which are principally a continuation of the work reported on in the 1949 report can be very brief. A few developments, however, not anticipated originally deserve special mention.

2. Photography of the spectrum and wave-length measurements. The photography of the spectrum was continued with a new tube obtained in April with the cooperation of Dr. Tomkins at Argonne. More will be said about this tube under Section 4. It was hoped that the tritium concentration in this tube would be better than 99%. This for all practical purposes would have yielded a pure T_2 spectrum with only the strongest TH lines present, which can easily be recognized.

A complete set of plates was obtained with this tube. This would have virtually concluded the photography of the spectrum. Unfortunately, while this tube showed a 99% tritium concentration at the time when it was filled, the tritium concentration gradually deteriorated while the tube was operated. The set of plates thus obtained, while superior to any obtained previously, was not good enough to differentiate between T_2 and TH lines except for the more prominent ones. The problem of assigning each observed line to its proper molecule (T_2 , TH or H_2) still remains unsolved.

Considerable delay was experienced in the photography of the spectrum because of difficulties in obtaining proper photographic plates. The delivery time was generally more than three months. Some plates ordered January 3, 1950 have not been received yet. These are plates sensitive for the wave-length region between 10,000 and 12,000 Å. Accordingly it has not been possible to obtain new wave-lengths in this region.

We have tried to anticipate our needs as much as possible and stock a large enough number of plates so that similar delays can be avoided in the future. This, of course, has as consequence that a certain number of plates will spoil before they can be used as the nature of the work makes it impossible to anticipate all needs exactly.

Steady progress has been made with the wave-lengths measurements. Most of the spectrum between 3000 and 9000 Å now has been measured on two plates. As soon as plates of pure T_2 are available a beginning can be made with the compilation of the final tables. While in the beginning of the work the analysis often was handicapped because of inadequate measurements in some regions of the spectrum, there are now adequate measurements throughout the spectrum.

3. Molecular spectrum of hydrogen in the presence of helium. When a tube is filled with a mixture of about 200 mm helium and 0.5 mm hydrogen and a low current discharge passed through, the resulting spectrum is the molecular spectrum of hydrogen with very pronounced modifications. All higher vibrational states are suppressed so that only the bands from $V = 0$ remain (see Report NYO-692 for further details). Furthermore the rotational temperature is considerably higher than in an ordinary discharge so that each band has a larger number of rotational lines.

This modification was well known for H_2 but no extensive use was made of it for the classification of new lines.

We obtained the D_2 spectrum in the presence of helium and the modifications were so pronounced that they helped greatly in unravelling some complicated parts of the spectrum. Figure 1 shows a part of the D_2 spectrum in the infrared near 8600 Å. The upper spectrum is the D_2 spectrum modified by helium. It shows nothing but the $0 \rightarrow 0$ band of the $3p^3\Sigma^- \rightarrow 2s^3\Sigma^-$ system. The lower spectrum on the other hand which is obtained with an ordinary discharge shows lines of many other bands which originate from higher vibrational levels. Another example is Figure 1 of Report NYO-692. Dr. Cunningham made extensive use of these data for the analysis of the higher electronic states. He also succeeded in revising the classification of the very complicated $3d^3\Sigma^-, \Pi, \Delta \rightarrow 2p^3\Pi$ bands. These had been analyzed previously and it had been realized that the analysis was not satisfactory in all respects. There had been no way to find a better analysis. With the help of the new data considerable changes were made and it is felt that this system is now in good shape.

With the success in D_2 of the spectrum modified by helium it became advisable to try the same technique with T_2 . A tube previously used with about 85% tritium was returned to Argonne where Dr. Tomkins filled it with the appropriate mixture of 200 mm helium and 0.5 mm tritium.

Although this tube had certain drawbacks as it could not be completely purified because of the short supply of tritium, it gave some very satisfactory spectra which showed the designed changes for the principal band system. A promising start in the analysis of the $3d^3\Sigma^-, \Pi, \Delta \rightarrow 2p^3\Pi$ bands for TH and T_2 was possible on account of this.

4. The problem of obtaining pure tritium. The importance of obtaining pure tritium for our work has been emphasized several times. In the beginning no samples with high enough tritium concentration were available. Arrangements were made at Argonne to have the available material further purified to obtain a sample with a tritium concentration of 99% or better (the rest being ordinary hydrogen). Dr. B. Weinstock at Argonne succeeded in doing this by repeated passage through palladium.

In April 1950 the author spent a few days at Argonne in order to assist Dr. Tomkins in filling a discharge tube with this sample. The electrodes were outgassed in an induction furnace, the quartz of the tube in a resistance furnace. Subsequently the tube was further cleaned with a powerful helium discharge. Even with these precautions the tube still showed traces of impurities when the tritium was admitted. This was similar to all previous experiences. The tritium concentration,

which was measured by comparing photoelectrically the intensity ratio of $T\alpha$ and $H\alpha$, showed in the beginning effects of dilution. After several fillings while the tube was run at very high currents, the measured tritium concentration exceeded 99% and also the impurities had disappeared. When after several hours running no further change could be observed the tube was sealed off.

When this tube was used in Baltimore the observed tritium concentration gradually dropped. This can only be due to hydrogen which is liberated slowly in the tube with continued operation. The parts chiefly responsible are probably the electrodes, and there is definite evidence that they play an important part. There is also the palladium valve which originally has a large quantity of hydrogen dissolved. This is gradually replaced by tritium, and great care was taken to use a valve which had been sufficiently treated by heating it in vacuum before being used to admit tritium. As the tube is sealed in glass its whole length cannot be heated and, therefore, there are parts which cannot be outgassed adequately and from which later hydrogen may diffuse into the tube. Finally the possibility that hydrogen may be released from the tube walls where it was adsorbed as water vapor cannot be entirely excluded.

It is rather difficult to deal with these sources of contamination because of the small amounts of tritium that must be used. There are good reasons to believe that the following changed procedure in filling and handling the tube will overcome most if not all these difficulties. The essential steps were suggested by Dr. E. Robinson, of the Los Alamos Scientific Laboratory.

The palladium valve is entirely done away with which eliminates this source of contamination. The tritium is stored as UT_3 . Uranium turnings are first converted into UH_3 by having them react with hydrogen at the proper temperature. The hydrogen is then driven out by heating the UH_3 to a sufficiently high temperature in a high vacuum. The hydrogen can be driven out completely this way. The activated uranium is then allowed to react with tritium and be converted into UT_3 . When the tube is used the uranium tritide is heated to the temperature at which the equilibrium pressure is the desired gas pressure.

This procedure should eliminate other difficulties, which hitherto have produced uncertainties. One of the difficulties was a lack of knowledge of the gas pressure in the tube. In order to avoid contamination and also in order not to complicate the tube unduly and thus make it unsuitable for being shipped from one laboratory to another, it was deemed not feasible to employ a pressure gauge with the sealed off tritium tubes. Because of the gas cleaned up in the electrodes the original pressure was usually not maintained for very long. The approximate pressure could be estimated roughly from the character of the discharge and when the gas pressure was considered too low new gas was admitted through the palladium valve.

This ignorance of the exact pressure had two very undesirable effects. These were of little importance at the beginning of the work, but made themselves felt more and more when attempts were made to work with high purity tritium and also when the finer details of the spectrum came into the scope of interest.

In the first place due to the circumstances mentioned above, it was not always possible to prevent the pressure in the discharge tube from getting too low. When the tube is operated with fairly high power, the electrodes become

very hot with low pressure and will give off impurities. Part of these impurities is hydrogen which will contribute to the dilution of the tritium. There are other impurities which may obscure the spectrum and which are discussed in Section 5.

The second undesirable effect of varying pressure makes itself felt when intensity measurements are made. The relative intensities are very sensitive to pressure changes. If the pressure is unknown and particularly when it varies during the measurements the intensity measurements lose much of their significance and their interpretation becomes uncertain.

The tritium pressure for gas in equilibrium with heated uranium tritide is known as function of the temperature of the uranium tritide. By measuring this temperature one can thus determine the gas pressure in the tube. Furthermore if the temperature of the tritide is kept constant the gas pressure remains automatically independent of any gas cleanup that might occur in the discharge.

There are other minor advantages and some possible minor disadvantages which should reveal themselves when such a tube is actually operated.

During the author's stay at Los Alamos this summer a tube was filled by Dr. E. Robinson and operated for some time without the possibility, however, for spectroscopic observations. Particular care was taken to outgas the electrodes in an induction furnace. The procedure appeared to be very successful, but unfortunately when the tube was sealed off it turned out that a defective quartz to pyrex seal made it unusable. Furthermore the contamination with tritium made it impossible to have this tube repaired.

I have every assurance from the persons concerned at Los Alamos for co-operation in getting a new tube filled. When this tube is received here it may turn out that it meets all the requirements and may be used for the final experiments.

Should it turn out that notwithstanding all precautions some progressive contamination occurs when the tube is being used, the most reasonable way to remedy this situation is as follows. After the tube has been used long enough so that an equilibrium in the electrodes and tube walls is established between the original hydrogen and the tritium, in other words when most of the hydrogen in the electrodes has been replaced by tritium, the gas filling is removed and replaced by a fresh one of the highest purity. The possibilities for further dilution have been eliminated so that very high purity tritium will remain. No tritium is lost in this way as all the tritium from the discarded sample may be recovered.

After such a tube has been used for obtaining the tritium spectrum, it, or a similar tube, may be filled with a mixture of tritium and deuterium in order to obtain the TD spectrum at its best development.

5. Impurities. In our previous report (JHU-4) the presence of impurities in the sealed off tritium discharge tubes was briefly discussed.

Some new experiences with impurities which were obtained with the last tube (initially containing 99% tritium) are worth recording as they throw some light on the general problem of impurities in gas discharges.

This tube was first operated with moderate currents (less than 0.5 A) for several weeks. Only the usual traces of impurities showed in the spectrum.

When the current was increased to 1.5 A, which was probably accompanied by a reduction in pressure due to cleanup of the gas, the character of the discharge changed completely after some time. This could be seen easily by a change in color which now became bluish. A pocket spectroscope showed that in the visible the T_2 spectrum had disappeared completely and was replaced by what were apparently strong CO and C_2 bands. The electrodes had become very hot and evidently enough CO had been driven out of the electrodes to have the discharge chiefly carried by CO. This gas was liberated notwithstanding that during several weeks of operation no trace of CO had shown in the spectrum.

It seemed desirable to investigate this very startling behavior of the tube. It turned out that besides CO and C_2 bands, also the OT and CT bands appeared with great intensity but that under these conditions the T_2 bands were entirely absent or very weak though the Balmer lines always remained. It soon was found that when the current was reduced, the CO spectrum could be made to disappear completely. The T_2 spectrum would then reappear with its former purity. It was possible to change in this sealed off tube, without addition of any further gas, from a pure T_2 spectrum to the CO + CT + OT spectrum and vice versa. The only explanation for this behavior is that at low enough electrode temperatures the CO is driven into the metal completely but can be driven out again if the temperature becomes sufficiently high. When CO forms a considerable fraction of the total gas the discharge is almost entirely carried by CO, CT, and OT, and the T_2 spectrum disappears.

While the tube was giving essentially the CO spectrum, the opportunity was used to obtain photographs of the OT and CT bands which should be adequate for the analysis of these bands if this should be desired.

The prospect of using T_2 obtained from the decomposition of UT_3 brings up the possibility of contamination by uranium lines. Such a contamination might be expected if short lived intermediate volatile compounds of uranium and tritium would be formed and find their way into the discharge tube.

As the uranium spectrum rivals the tritium spectrum in complexity, the presence of such impurity lines would not easily be detected unless comparison plates are available.

We photographed, therefore, the uranium spectrum with the large spectrograph with and without the presence of hydrogen. There was no spectroscopic evidence for any diatomic uranium hydride. One striking feature was that the atomic hydrogen lines were very diffuse. This diffuseness seemed to be due neither to a normal Doppler effect nor to a Stark effect. The possibility that this is due to a hydrogen atom attached to uranium cannot be excluded although more positive evidence is required to make this reasonably sure.

6. Intensities. As emphasized before, reliable intensity measurements are very important for the analysis of the spectrum. Even more so are the changes with different discharge conditions. Extensive use has been made of this in the work so far achieved. If the changes are large they can easily be recognized

qualitatively on microphotometer traces of suitable plates. These have been used as a matter of routine throughout.

Better measurements are obtained by direct photoelectric measurements in the spectrograph. These will show also small intensity changes and will make possible quantitative conclusions. The technique for such measurements has been worked out and sample measurements have been made successfully. In order that such measurements be meaningful they must be made under constant well-defined discharge conditions. The difficulties mentioned in Section 4 in measuring the pressure and keeping it constant in a sealed off T_2 tube have made the value of accurate measurements somewhat illusory.

The intensity measurements are tedious and time consuming. There seemed to be little point in carrying them out on a large scale unless they are made under the best possible conditions. There is every indication that the proposed new tritium tube will present suitable conditions for intensity measurements.

7. The molecular spectrum of He^3 . Complete sets of plates were obtained with the second He^3 tube obtained from Los Alamos mentioned in JHU-4. The work given in Appendix II of JHU-4 was repeated under improved conditions and has since been published. The analysis of further parts of the He_2^3 spectrum has been undertaken as time permitted.

The result of chief interest emerging from this is that He_2^3 is probably the only diatomic molecule where an influence of the nuclear spin on the fine structure of band lines in the visible can clearly be demonstrated. The ordinary triplet structure due to the electronic spin was partially resolved for He_2^3 by Mulliken and Monk (Phys. Rev. 34, 1530 (1929)). On our grating plates this same structure is resolved clearly for all bands ending on the $2p^3\pi$ state. For He_2^3 alternate rotational lines show different fine structures. The only fundamental difference between such states is the nuclear spin orientation. The nuclear spin does thus produce a noticeable effect on the energy levels.

This effect should be pursued further. The resolution with a large grating spectrograph is just near the limit of showing the effect. High resolution, such as may be obtained with an interferometer, is desirable. It is hoped that this can be obtained in the near future.

While originally there had been no intention of obtaining the He^3He^4 spectrum this nuclear spin effect makes it desirable to study some of the strongest bands of the mixed molecule. This will be done as soon as a suitable tube is available.

At the present time the chief limitations for the photography of the weaker He_2^3 lines are the presence of traces of impurities and the overwhelming intensity of the atomic lines which obliterate the weak molecular lines in the vicinity of the atomic lines.

The remedy for the first difficulty is a tube that is more carefully purified than the one used so far. We have been promised the cooperation of the Los Alamos Scientific Laboratory for obtaining such a tube.

The difficulties in the vicinity of the strong atomic lines can be overcome if the spectrum can be excited under such conditions that these are absent or very weak. Such conditions are known but they weaken the whole spectrum so much that it cannot be obtained with a spectrograph of high enough resolution.

In work carried out in our laboratory not directly related to this project we have tried to clear up the conditions under which diatomic helium molecules are produced in a discharge. This work has given many new results but is still unfinished.

Mr. Parkinson has found in the course of this work that the molecular spectrum can be obtained with great intensity practically free from the atomic lines in the vicinity of the electrodes in an A.C. discharge at a frequency of a few kilocycles per second.

A study is now being made of whether this type of discharge may be used to get improved photographs of the molecular spectrum of helium.

8. Spectroscopic analysis for the purity of tritium or deuterium. The intensity ratio of $T\alpha$ to $H\alpha$ is a measure for the tritium concentration in a sample. The intensity ratio would be exactly equal to the ratio of the tritium and hydrogen concentration if there were not certain complicating circumstances. In our previous report (JHU-4) we showed that in a sealed off tube the intensity ratio may vary widely with current and this was attributed to preferential absorption in the metal electrodes. Presumably the intensity ratio is still an indication of the tritium concentration of the free gas in the tube. Further experiments confirmed this.

The photoelectric measurement of the intensity ratio of $T\alpha$ to $H\alpha$ presents a very convenient and fast method for the determination of the tritium concentration. Before this method can be recommended without reservations, however, for practical use it is desirable to find out with what accuracy the intensity ratio actually represents the ratio of the concentrations.

This became of some practical importance when we were asked to cooperate with the Knolls Atomic Power Laboratory to work out the best conditions for the spectroscopic method of tritium assay under routine working conditions.

Factors that may affect the intensity ratio are:

1. Dilution by hydrogen in the discharge tube;
2. Self-absorption of the lines;
3. Difference in sharpness of the two lines;
4. Preferential excitation of one of the two isotopes.

The dilution by hydrogen from the walls of the tube is more serious than usually assumed even when every reasonable attempt had been made to degas the tube. This is apt to startle anyone who has had no actual experience with such phenomena and then is usually the chief source of trouble. It is, of course, also present in any other method which uses small quantities of gas, particularly in the presence of an electrical discharge. It is present when a mass spectrometer is used and is even more difficult to eliminate in that case.

Elimination of metal electrodes and circulation of the gas will get rid of the dilution effect.

The possibility (4) of a preferential excitation of one of the isotopes would also be present with the use of the mass spectrometer. (2) and (3) are typical spectroscopic effects, which should be small unless one works under extreme conditions.

The various effects make themselves felt as a variation of the intensity ratio with the same gas sample if the pressure or the discharge conditions are changed. In the first place metal electrodes should be avoided which necessitates an electrodeless high frequency discharge. In order to be able to study the influence of the individual factors separately, the following system was designed.

The gas is circulated continuously with a mercury diffusion pump capable of operating at pressures up to 10 mm. The pressure in the discharge tube is changed by the adjustment of two needle valves which control the flow of gas into the discharge tube from a reservoir and away from the tube to the pump. One is thus assured that always the same isotopic mixture is used. There are three discharge sections in series one to be viewed from the side, the other two end on. Of the latter one is clear glass, the other one silvered. The necessary traps and pressure measuring devices complete the system. It has been completed and tested and is ready for operation.

9. Instrumentation for measuring the isotopic constitution of hydrogen samples. It often becomes necessary to obtain quickly the deuterium concentration in a D-H mixture or the tritium concentration in a T-H mixture. Sometimes a qualitative estimate is sufficient, in other instances an exact measurement is required. The spectroscopic method when properly used is well adapted for both cases.

It has the disadvantage, however, that rather elaborate spectroscopic equipment is required to resolve H_{α} and D_{α} (separation 1.78 Å) or H_{α} and T_{α} (separation 2.38 Å). Spectrographs capable of resolving these lines are usually not portable and this may present difficulties if the deuterium or tritium installation is not in a spectroscopic laboratory. The testing of the gas in whatever installation it is to be used is greatly to be preferred to taking small samples for test purposes from it. This latter procedure is apt to give faulty results due to dilution.

As the resolving power required for the separation of the isotopic components H_{α} , D_{α} , T_{α} is not large (only of the order of about 3,000) it should be possible to achieve the desired results with rather simple instruments.

After the consideration of several other possibilities the following solution seemed to present the best chances for success.

An interference filter with a band width of about 50 Å may be used to isolate H_{α} and D_{α} and T_{α} from the rest of the spectrum. This will be very effective unless special efforts have been made to keep the intensity of the Balmer lines down in favor of the molecular lines. Under such circumstances there might be molecular lines present in the vicinity of H_{α} of sufficient strength to interfere with the proper use of the filter. It is usually not difficult to avoid this condition.

This filter is then combined with an interferometer which gives a free spectral range of a few Angstrom Units. This means a very small gap between the plates. As the quality of the interferometer does not have to be very high because of the modest resolution required, this should present no difficulties.

The interference ring system of $H\alpha$ is then separated by rings of $D\alpha$ and $T\alpha$ and from the relative intensity of the rings the deuterium or tritium concentration may be determined.

At a visit to Baird Associates in Cambridge, Mass. on October 5 this matter was discussed with Dr. B. Billings, of Baird Associates, who has considerable experience in making interference filters and interferometers. Dr. Billings expressed the opinion that a simple and relatively inexpensive instrument having the required properties could be made.

10. General outlook. On the whole the work has progressed more or less as planned. The task of photographing the spectrum and measuring the wave-lengths has been carried through without delay.

For the year ahead the chief task will be the compilation of the final wave-length tables. The beginning of this has been somewhat retarded because of the lack of a tube with pure tritium. This is now in sight, however. Such a tube will also make possible the photography of the TD spectrum and definite intensity measurements in the T_2 spectrum.

As before a moderate amount of work on D_2 and He_2^3 will be carried out along with the main work on T_2 .

At the present time the experimental work on T_2 has been interrupted because of the request for help on the development of a spectroscopic method for determining the tritium concentration. It is expected that this interruption is only temporary and will be over when we receive the new tritium tube. The new tube also will make it possible to obtain reproducible intensity measurements.

In the meantime there has been no interruption in the program of wave-length measurements and analysis.

If matters proceed well, particularly if we shall get a successful T_2 tube in the near future, the wave-length measurements of the T_2 spectrum should be substantially finished at the end of 1951.

11. Publications and Technical Reports.

G. H. Dieke and E. S. Robinson, The Molecular Spectrum of He^3 , Phys. Rev. 80, 1-5 (1950).

G. H. Dieke and F. S. Tomkins, The $3p^3\Sigma \rightarrow 2s^3\Sigma$ Bands of TH and T_2 , Report No. NYO 530. Submitted to the Physical Review for publication.

S. P. Cunningham and G. H. Dieke, Some higher electronic states in the molecular spectrum of hydrogen and its isotopes, Report No. NYO 692. (Submitted together with this report.)

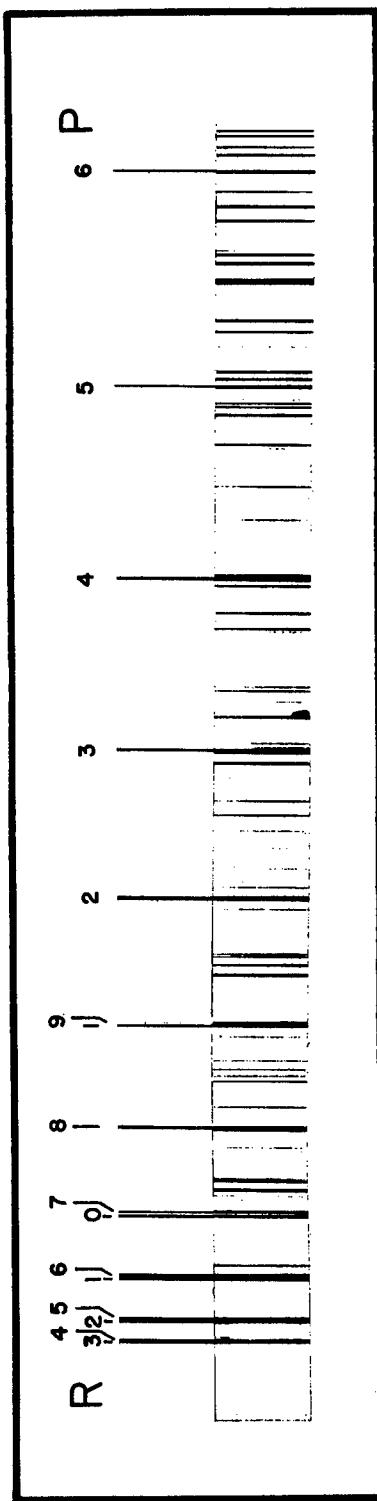


Fig. I

O \rightarrow O band of $3p^3\Sigma \rightarrow 2s^3\Sigma$ system of D_2 near 8600 A.

Top: Modified by helium.

Bottom: Ordinary discharge.